# RAMAN SPECTRA OF ORTHO- AND PARACHLORO-ANISOLE IN THE SOLID STATE AT −180°C*

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(*Received, February* 2, 1960)

Plate III

**ABSTRACT.** The Raman spectra of ortho- and parachloroanisole have been studied in the liquid state and in the solid state at −180°C. It has been observed that in the case of parachloroanisole the components of each of the doublets 625 and 638 $cm^{-1}$ and 1584 and 1596 $cm^{-1}$ coalesce to form a single line of Raman shift 640 $cm^{-1}$ in the former case and 1603 $cm^{-1}$ in the latter case. When the liquid is solidified a new line 3026 $cm^{-1}$ also appears in the spectrum. Besides these changes three new low frequency Raman lines 60, 92 and 132 $cm^{-1}$ also appear with solidification of the liquid.

In the case of orthochloroanisole no appreciable changes take place in the spectrum and no new low frequency lines appear with the solidification of the liquid. It has been concluded from these results that in the case of the ortho compound the $OCH_3$ group is probably chelated to the adjacent chlorine atom and therefore the formation of associated groups is not possible in the solid state. Such groups are, however, formed when the para compound is solidified and the new low frequency lines observed in this case are attributed to such groups of molecules.

## INTRODUCTION

Since the discovery of new low-frequency Raman lines in the Raman spectra of some substituted benzene compounds in the solid state by Gross and Vuks (1936) many workers have investigated the Raman spectra of a large number of such solidified benzene compounds at different temperatures (Sirkar, 1937; Mazumder, 1949, Ray, 1950a,b, 1951, 1952, Biswas, 1954,a,b,c, 1955a,b,c, 1956a; and others). It has been concluded by these workers from the results obtained by them that the low-frequency Raman lines originate from vibrations in small groups of molecules formed by the attachment of the individual molecules to neighbouring molecules through weak linkages and that these lines cannot be attributed either to angular oscillations of the molecules about their axes as suggested by Kastler and Rousset (1941) and by Bhagavantam (1941) or to translational lattice oscillation as suggested by Gross and Vuks (1936). Generally, halogen substituted benzene compounds yield strong low-frequency Raman lines in the solid state and it has been pointed out that the formation of weak intermolecular bonds is more probable in such cases than in the molecules in which no such halogen atom

*Communicated by Prof. S. C. Sirkar.

is present as a substituent. In certain disubstituted benzene compounds, such as chlorophenol, chloroanisole, etc., there is rotational freedom of the OH or $OCH_3$ group about the C—O bond, but the relative positions of the halogen atom and the other substituent have influence on such rotational freedom. It would be interesting to find out whether the formation of intermolecular linkages in the solid state and the consequent production of low-frequency Raman lines are influenced by relative positions of the two substituents in such cases. As a preliminary investigation of this problem, the Raman spectra of ortho- and parachloroanisole in the solid state at —180°C have been studied and the results have been compared with those for the liquids.

## EXPERIMENTAL

The liquids were of chemically pure quality supplied by British Drug House. They were further purified by distillation under reduced pressure. While recording the spectra due to the liquids a strong continuous fluorescence in the visible region was observed. Hence, to reduce the intensity of this fluorescence a second photograph of the spectrum was taken in each case using Rhodamine 6 GBN filters which cut off 4046Å group of mercury lines. The fluorescence was found to be stronger in the case of orthochloroanisole than in the case of the para compound.

In order to record the Raman spectra of the compounds in the solid state attempt was made to obtain a homogeneous solid mass by cooling the liquid slowly so that the stray light due to diffuse reflection from the inner portion of the solid could be reduced considerably. The experimental arrangement in this case was the same as that used by Biswas (1954). The Raman spectra were recorded on Ilford Zenith plates using a Fuess glass spectrograph giving a dispersion of about 11 Å in the region of 4046Å. The polarisation of the Raman lines due to each of the compounds was also studied in the usual manner, but in the case of the ortho compound a freshly prepared 5% $NaNO_2$ solution was used as a filter in order to avoid the continuous fluorescence in the regions from 4358Å to 4916Å.

## RESULTS AND DISCUSSION

The spectrograms are reproduced in Plate III. The Raman frequencies of the lines are given in Tables I and II. The frequencies reported for the liquids by previous workers are also included in the tables. The states of polarisation of the Raman lines due to the compounds are indicated in the respective tables by the usual symbols $D(\rho \geqslant 6/7)$ and $P(\rho < 6/7)$, $\rho$ being the depolarisation factor.

(*a*) *Parachloroanisole* :

It can be seen from Table I and Figs. 1(a) and 1(b) that the following changes take place when this liquid is solidified and cooled to —180°C.

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PLATE III A

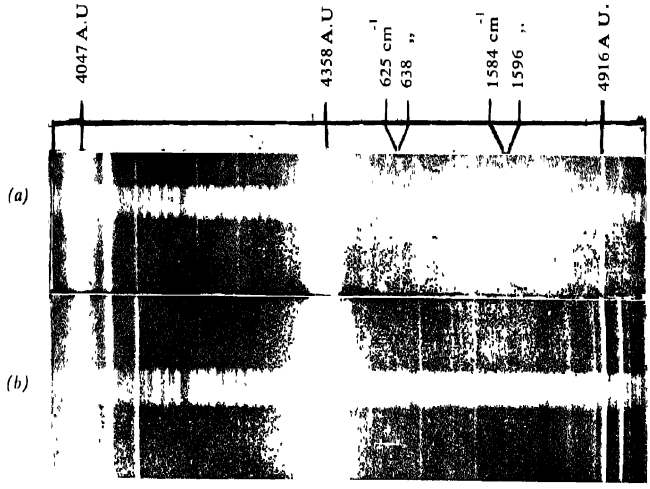


Fig. 1

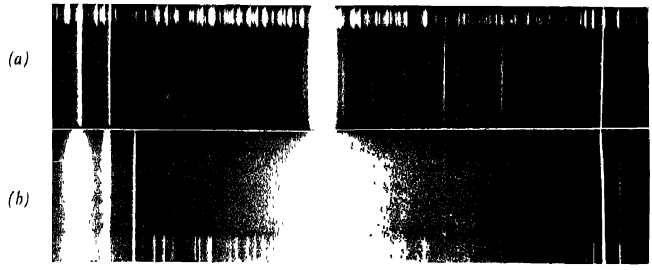


Fig. 2

Fig. 1. *(a)* Raman spectra of parachloroanisole liquid at 30°C
*(b)* ,, ,, parachloroanisole solid at −180°C
Fig. 2. *(a)* ,, ,, orthochloroanisole liquid at 30°C
*(b)* ,, ,, orthochloroanisole solid at −180°C

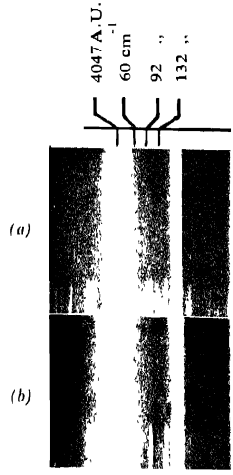


Fig 3

Fig. 3. *(a)* Raman spectra of parachloroanisole solid at −180°C, showing low-frequency lines
*(b)* orthochloroanisole solid at −180°C

Three new Raman lines with Raman shifts 60, 92 and 132 $cm^{-1}$ appear in the spectra due to the solid (Fig. 3a), the line 92 $cm^{-1}$ being the strongest. Further, some of the prominent Raman lines of the molecule undergo changes in position and intensity with the solidification. The intensity of the doublet 625 $cm^{-1}$ and 638 $cm^{-1}$ is reduced appreciably and the two lines coalesce to form a single line 640 $cm^{-1}$. The line 799 $cm^{-1}$ shifts to 804 $cm^{-1}$ and the lines 1584 $cm^{-1}$ and 1596 $cm^{-1}$ coalesce to form a single line at 1603 $cm^{-1}$. Finally, a new strong line at 3026 $cm^{-1}$ appears in the spectrum due to the solid.

The diminution in the number of Raman lines with the solidification of the liquid may be due to the fact that there exist in the liquid state two types

TABLE I

Parachloroanisole. $\Delta\nu$ in $cm^{-1}$

| Liquid | | | Solid at −180°C |
|---|---|---|---|
| Hertz (1947) | Present author | | Present author |
| | | | 60 (3) |
| | | | 92 (8b) |
| | | | 132 (3) |
| 143 (3) ? | 150 (0) ? | | 145 (3) |
| 212 (3) | 218 (1b) | P | 225 (0) |
| 309 (4) | 313 (3) | P | 313 (2) |
| 335 (4) | 335 (4) | D | 335 (1) |
| 366 (5) | 367 (4) | P | 367 (2) |
| 498 (1) | | | |
| 625 (5) | 625 (5) | P | |
| 636 (5) | 638 (3b) | P | 640 (1) |
| 698 (3) | 695 (0) | D | 695 (0) |
| 797 (10) | 799 (10) | P | 804 (10) |
| 829 (1) | 826 (0) | P | |
| 1006 (3) | 1005 (1) | P | 1005 (1) |
| 1034 (1) | 1035 (0) | P | |
| 1091 (8) | 1091 (8) | P | 1094 (3) |
| 1100 (1) | | | |
| 1168 (3) | 1170 (4b) | P | 1169 (2) |
| 1181 (3) | 1182 (3) | P | 1188 (1) |
| 1244 (3) | 1243 (3) | P | 1250 (0) |
| 1292 (3) | 1293 (4b) | P | 1299 (2) |
| 1404 (1) | | | |
| 1440 (3) | 1443 (2) | P | |
| 1458 (3) | 1459 (3b) | P | 1458 (1) |
| 1492 (1) | | | |
| 1580 (4) | 1584 (3) | D | |
| 1594 (7) | 1596 (6b) | D | 1603 (5) |
| 2836 (4) | 2844 (4) | P | 2844 (2) |
| 2937 (2) | 2938 (2) | P | 2838 (1) |
| 3010 (1) | | | 3026 (5) |
| 3064 (6b) | 3064 (4b) | P | 3064 (5) |
| 3075 (6b) | 3073 (5) | P | 3073 (4) |

of molecules, namely, monomers and dimers, the latter being formed through weak intermolecular bonds between two neighbouring molecules. When the liquid is solidified probably all the molecules are transformed into small groups of molecules formed by association of the monomers and dimers through virtual linkages. The fact that the lines 625 $cm^{-1}$ and 638 $cm^{-1}$ change to a single line 640 $cm^{-1}$ with the solidification of the liquid shows that these virtual linkages take place between Cl and H atoms of the two neighbouring molecules respectively. As an example of such small splitting of some of the Raman lines with formation of dimers, mention can be made of the change in the Raman spectra of the solution of pyridine with dissolution in alcohol (Kastha, 1956). The spectra due to pure pyridine gives two Raman lines at 995 $cm^{-1}$ and 1029 $cm^{-1}$ of almost the same intensity, but when the liquid is dissolved in alcohol the former line becomes very weak. This is due to the fact that the non-bonding electron of the N-atom of pyridine forms a bond with the OH-group of the neighbouring alcohol molecules. In the present case also of the two lines 625 $cm^{-1}$ and 638 $cm^{-1}$, the first one may be due to the monomers and the second one due to the dimers, and with solidification the former line disappears owing to formation of groups of molecules It is also found that a new line 3026 $cm^{-1}$ is produced when the liquid is solidified. This shows that probably the H-atom attached to the benzene ring is responsible for the formation of virtual linkages with the Cl-atom of the neighbouring molecules The disappearance of the line 1584 $cm^{-1}$ also leads to the conclusion that this line is due to monomers while the other line 1596 $cm^{-1}$ which persists in the solid state is due to the dimers.

(b) *Orthochloroanisole* :

On examination of the Raman spectra of orthochloroanisole in the liquid and solid states (Figs. 2a and 2b) it is found that no appreciable change takes place in the specturm when the liquid is solidified. Hence, the formation of dimers in the liquid is not observed in this case. This may be due to the fact that the Cl-atom, which is the reactive atom for the formation of the dimers, is chelated to the $OCH_3$ group, and therefore, it is no longer able to form a virtual bond with neighbouring molecules.

Tables I and II and also Figs. 3a and 3b show that *p*-chloroanisole produces three strong new low-frequency lines 60, 92 and 132 $cm^{-1}$ in the solid state at $-180°C$ while the ortho compound under the same condition does not produce any new line in this region. It has already been pointed out that in the para compound groups of molecules are formed while in the case of the ortho compound even in the solid state all the molecules remain as monomers. These facts show that the new lines in the low frequency region produced by the para compound in the solid state are due to groups of molecules Had these lines been due to lattice vibrations they would also be produced by the ortho compound. The

TABLE II

Orthochloroanisole. $\Delta\nu$ in $cm^{-1}$

| Liquid | | Solid at −180°C |
|---|---|---|
| Hertz (1946) | Present author | Present author |
| 160 (5bd) | 160 (6b) D | 165 (2b) |
| 204 (3b) | 202 (4) D | 202 (2b) |
| 288 (1) | 290 (2vb)P | |
| 410 (5b) | 407 (8) P | 407 (2) |
| 444 (1) | 440 (0) | |
| 493 (6) | 493 (8) P | 493 (3) |
| 546 (0) | 550 (0) P | |
| 576 (1b) | 573 (3) D | 573 (0b) |
| 685 (8) | 687 (8) P | 692 (6) |
| 712 (1) | 708 (0) D | |
| 753 (1b) | 756 (1b) D | |
| 785 (1) | | |
| 796 (7) | 798 (6) P | 798 (8) |
| 844 (0) | | |
| 925 (0) | | |
| 995 (2) | 995 (1) | |
| 1025 (2) | 1025 (1) P | |
| 1041 (10) | 1038 (10) P | 1038 (8) |
| 1065 (1) | | |
| 1092 (1) | 1091 (0) | |
| 1133 (1) | 1130 (1) | |
| 1162 (5) | 1164 (6) D | 1164 (1b) |
| 1183 (3) | 1181 (2d) P | 1180 (0) |
| 1208 (0) | | |
| 1250 (6) | 1253 (5) P | 1257 (2) |
| 1274 (2) | 1271 (2) P | |
| 1300 (3) | 1299 (3) P | 1302 (1) |
| 1360 (0) | | |
| 1436 (1) | | |
| 1463 (1) | 1462 (2) D | |
| 1486 (2) | 1485 (3) P | 1484 (1b) |
| 1576 (5) | 1576 (7) D | 1576 (3) |
| 1588 (5) | 1588 (7) D | 1586 (3) |
| 2831 (2b) | 2833 (3b) P | 2833 (0) |
| 2948 (2) | 2948 (2b) P | |
| 3004 (8) | | |
| 3068 (8) | 3071 (9vb)P | 3073 (6) |
| 3076 (7b) | | |

results thus lead to the conclusion that the low frequency lines are due to vibrations in groups of molecules.

ACKNOWLEDGMENT

The author is indebted to Professor S. C. Sirkar, D.Sc., F.N.I. for his keen interest and constant guidance throughout the progress of the work.

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